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AGEING-TIME DEPENDENCE OF MECHANICAL PROPERTIES OF AN
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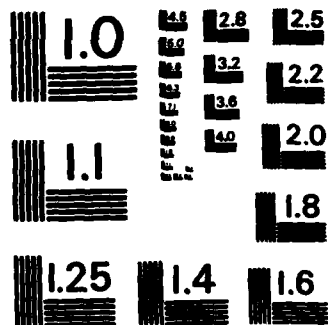
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AGEING-TIME DEPENDENCE OF MECHANICAL PROPERTIES
OF AN ELASTOMERIC GLASS

by

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abstract

Compressive stress-strain curves of two different glasses of a polyurethane based elastomer have been obtained at 3 Kbar and -5.5°C as a function of ageing time. The glasses were formed by two different perturbation jumps of pressure and temperature. The shape and the size of the curves depended on the path and ageing time. Young's modulus increased with ageing time and represents a good mechanical parameter for determining relaxation of polymer glasses.



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INTRODUCTION

The relaxation of the polymer glasses has been the subject of intense investigation by many researchers in recent years(1-6). Main features that are involved in the phenomenon are rate dependence of cooling and heating, the asymmetrical changes of properties upon heating and cooling, the nonlinear recovery of

glass upon annealing below the glass transition point and the memory effect due to successive perturbation jumps. These features have been brought out by the time dependent changes of properties with respect to temperature perturbation. Since most of the experimental studies have been carried out at atmospheric pressure, the problem is essentially a three-dimensional one. When a polymeric liquid is subjected to a combination of perturbations by pressure and temperature, the problem is four dimensional and the glasses formed this way are expected have entirely new sets of relaxation spectrum. Only limited work has been done involving pressure and temperature(7-9).

In this paper, results of a study involving measurements of the mechanical properties of polymer glasses formed by perturbation of pressure and temperature as a function of ageing time are presented and discussed.

EXPERIMENTAL AND MATERIAL

Solithane 113 is a polyurethane elastomer made by reaction of castor oil with tolylene diisocyanate. It is composed of 50:50 volume % of resin and catalyst and has molecular weight between cross-links of 2000 g/mol. The density is 0.97 g/cm and the T_g at atmospheric pressure is about -20°C . The specimens for the compression tests are circular cylinders with 1/2 in. diameter and 1.0 in. height.

Compressive stress-strain tests were carried out at 3 Kbar and

-5.5 °C as a function of ageing time up to 10 hours after the glasses were formed by two different paths. Low Pressure Path (LP-Path) involved lowering temperature to -5.5°C and then increasing pressure to 3.0 Kbar and High Pressure Path (HP-Path) involved increasing pressure to 3 Kbar and then lowering temperature to -5.5°C as shown in Fig. 1. All temperature changes were made at a rate of 0.5 °C/min from room temperature (20 °C) and all pressure increases from atmospheric pressure at 0.25 Kbar/min. The stress-strain tests were carried out in an apparatus capable of containing pressures to 7 Kbar and temperatures from -100 °C to 100 °C with all internal sensors.

RESULTS AND DISCUSSION

The compressive stress-strain curves obtained at various ageing times for LP-Path and HP-Path glasses are shown in Fig. 2 and 3, respectively. The stress-strain curves clearly show path dependence as 0.5 hr. curve for HP-Path is much lower in the elastic modulus (E) and yield strength (σ , 2% off-set) (not shown) than that of LP-Path curve. The stress-strain curves shifted upward as functions of ageing time, exhibiting increased E and σ . Fig. 4 shows ageing time dependence of E . HP-Path curve of E crosses over LP-Path's.

It was determined that E represents indeed a measure of volumetric relaxation of the glasses, if one assumes an elastic relationship, $K = E/3(1-2\nu)$, holds throughout the relaxation process;

that is,

$$1/E = A \delta + 1/E_{00} \quad (1)$$

where $\delta = (V - V_{00})/V_{00}$, A a constant, and E_{00} the equilibrium modulus.

One can calculate the overall relaxation time(τ) for each path using Fig. 4, by

$$d(1/E_i)/dt = (1/E_i)/\tau \quad (i = 1, 2) \quad (2)$$

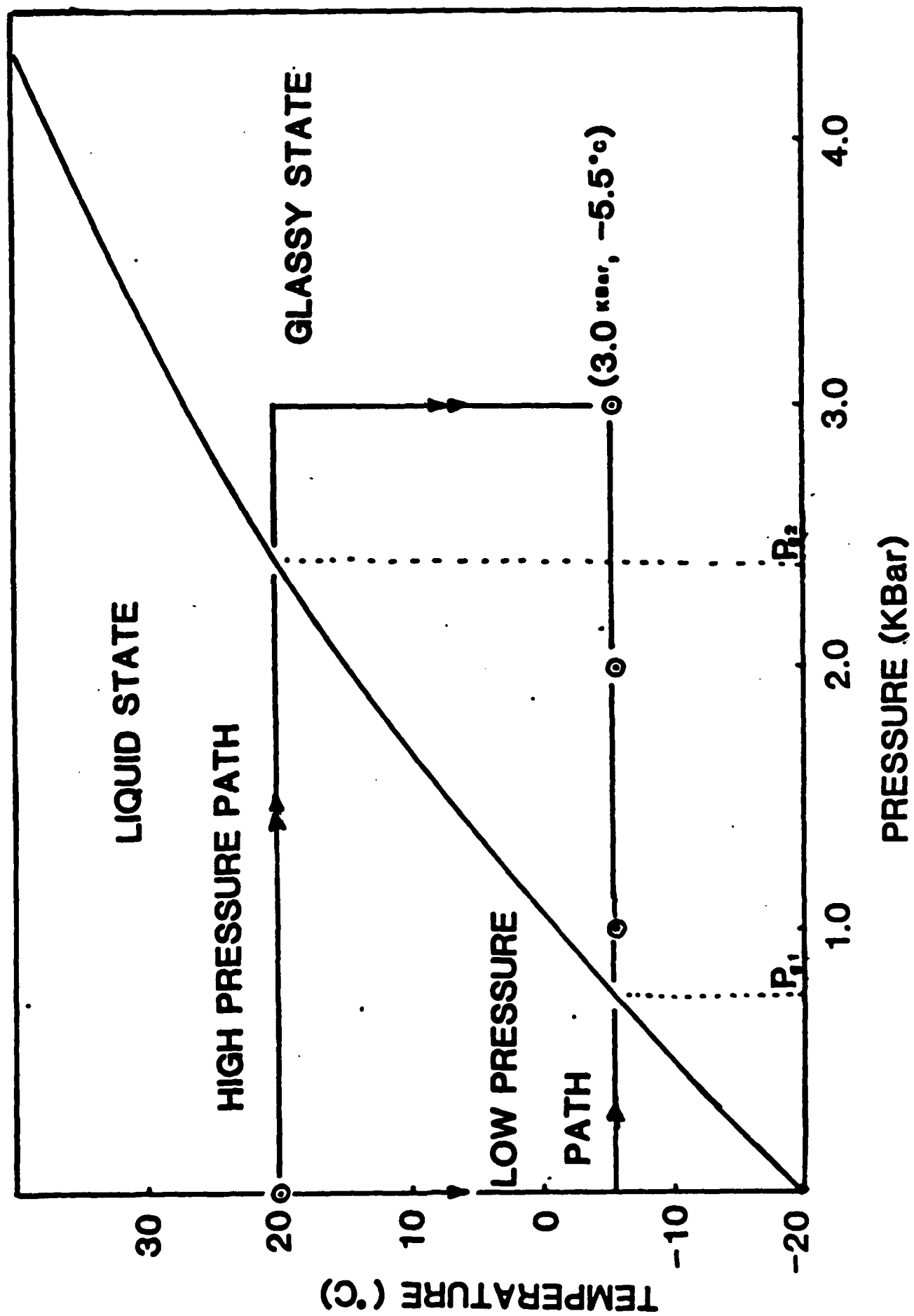
where 1 and 2 indicate HP-Path and LH-Path, respectively.

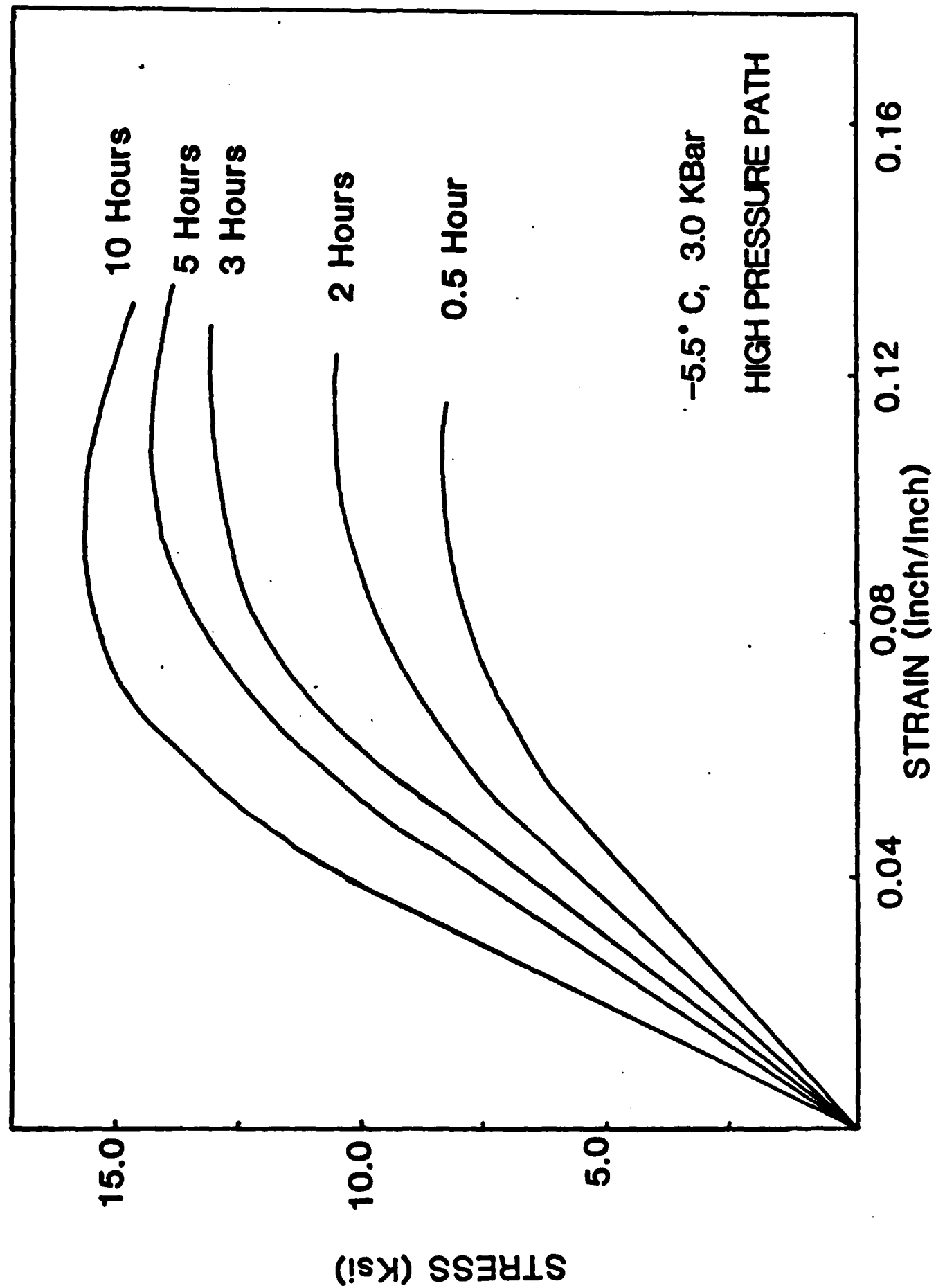
It is also clear from the experimental data(Fig. 4) that a spectrum of relaxation times exists at a point in P-T-t space, namely $P=3\text{Kbar}$ and $T=-5.5^\circ\text{C}$ for this study, and that the relaxation times depend on the pressure and temperature history. More Specifically it appears that the relaxation times depend also on the glass forming conditions. In other words, the memory effect influences the relaxation spectrum. A single physical parameter that is closely associated with the pressure-temperature history is the glass transition pressure(P_g). This would be equivalent to what others workers describes as the structural factor.

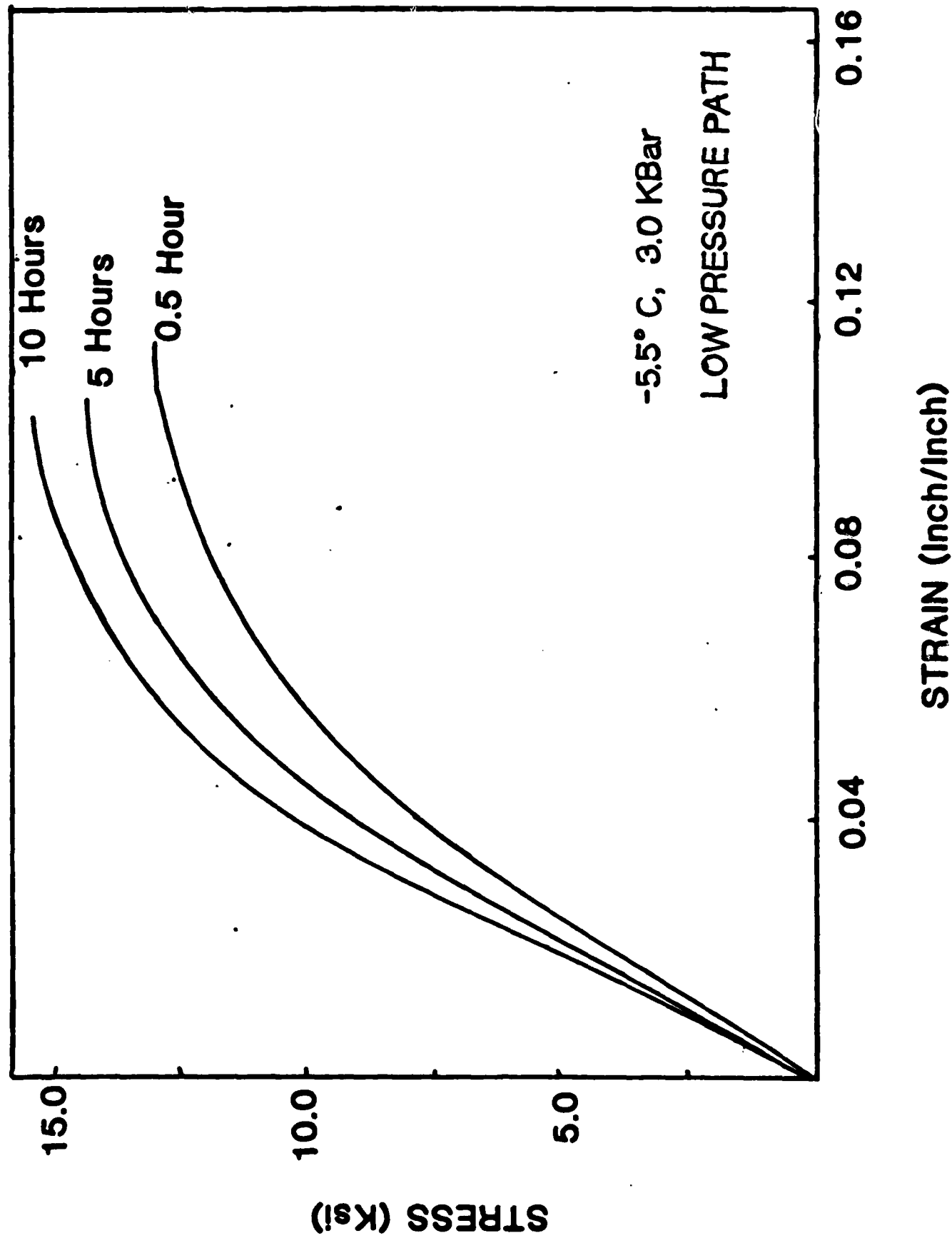
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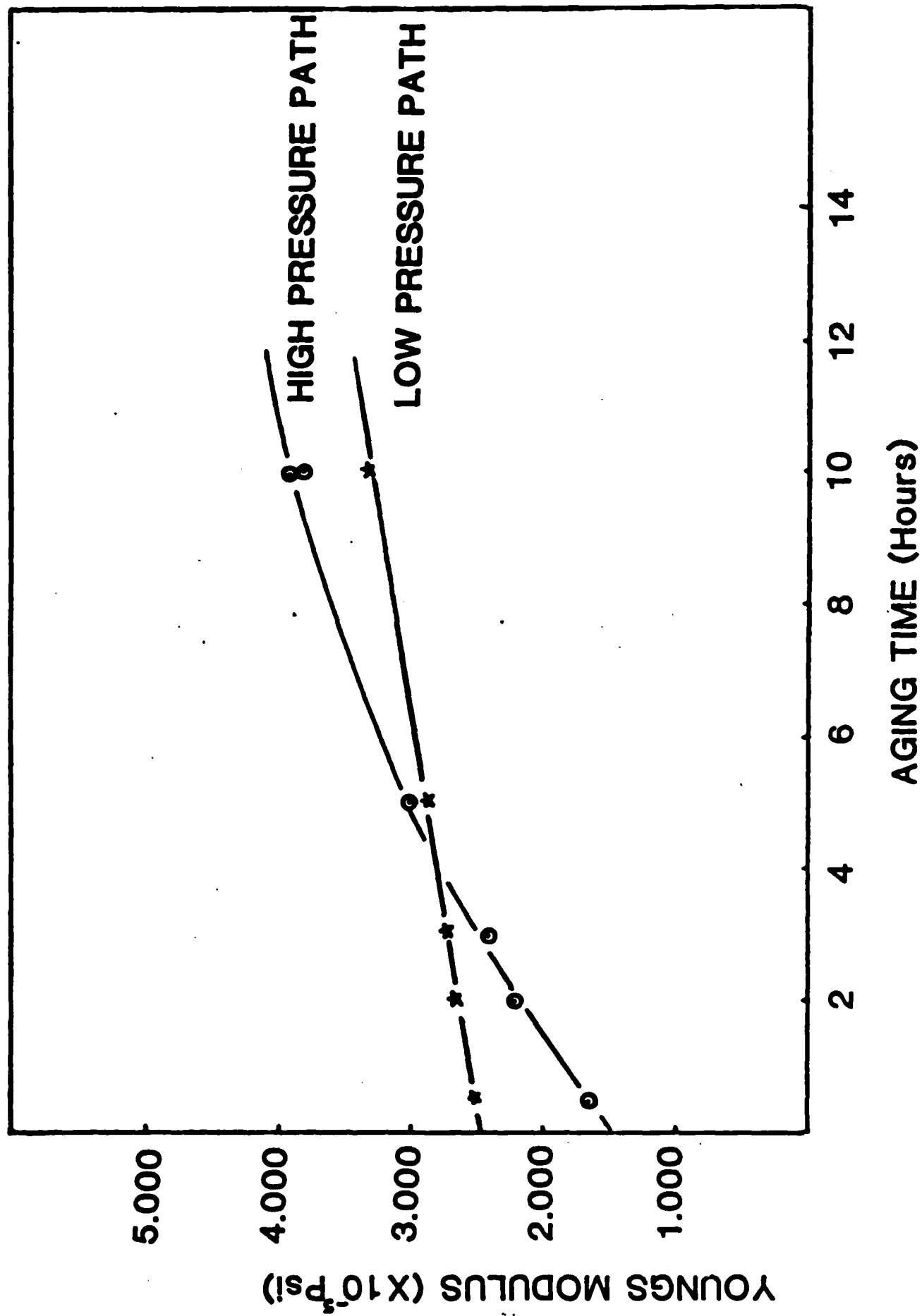
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